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Laboratory Measurement of Radionuclide Sorption in Solid Waste Storage Area 6 Soil/Groundwater Systems

H. A. Friedman
A. D. Kelmers

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LABORATORY MEASUREMENT OF RADIONUCLIDE SORPTION IN SOLID WASTE STORAGE AREA 6 SOIL/GROUNDWATER SYSTEMS

H. A. Friedman
A. D. Kelmers

June 1990

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ABSTRACT

Batch contact sorption tests were completed to measure the sorption of several radionuclides in Oak Ridge National Laboratory's Solid Waste Storage Area 6 (SWSA-6) saturated zone soil/groundwater system at a pH of near neutral. In the linear region of the sorption isotherms, sorption ratios for cesium, cobalt, and europium were typically near the analytical detection limit of >3000 L/kg. Strontium and uranium sorption ratios were lower, ranging from 50 to 75 L/kg. The SWSA-6 soil had a high sorption capacity for these elements; and competition for sorption sites, as evidenced by decreased sorption ratios, was not observed in tests with cesium, cobalt, and europium. Minor competition effects were noted for strontium and uranium. Several SWSA-6 unsaturated zone soils were tested; the sorption was markedly reduced in the case of cesium and cobalt. Scouting tests were performed to explore the effects of pH on europium and uranium and the effects of added organic reagents on europium sorption. Provisional sorption ratio values are recommended for use in modeling the mobility of these radionuclides in the SWSA-6 saturated zone.

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1. INTRODUCTION

The modeling of the migration of contaminants through low-level waste (LLW) sites conventionally involves the use of retardation factors to characterize the reduced mobility of the contaminants, relative to the groundwater flow rate, which results from sorption of the contaminants onto the soil (Lutton et al. 1982). The retardation factor, R_F (dimensionless), is derived from the expression

$$R_F = 1 + K_D(\rho/\theta) ,$$

where K_D = the experimentally measured sorption distribution coefficient (L/kg),

ρ = the rock bulk density (kg/L), and

θ = the porosity (dimensionless).

Other, more sophisticated modeling methodologies can also be applied to predict the mobility of contaminants (e.g., Pin et al. 1984); but these also require knowledge of the distribution coefficient.

To support modeling of the mobility of radionuclide contaminants in the Solid Waste Storage Area 6 (SWSA-6) disposal site at Oak Ridge National Laboratory (ORNL), we undertook a limited laboratory effort to measure the sorption ratio for some of the major radionuclides known to be present at the site (Boegly et al. 1985). Tests were run with Cs, Co, Eu, Sr, and U. We have chosen to call the sorption parameter measured by batch contact tests the "sorption ratio" rather than the distribution coefficient to avoid implying thermodynamic equilibrium. Most of the batch contact tests were carried out at near-neutral pH because groundwater samples from wells in SWSA-6 usually have pHs in the range of 7.4 to 7.7 (Boegly et al. 1985). In most cases, sorption isotherms were run to explore the effect of the radionuclide concentration on the sorption ratio. A few tests were run to examine the effect of pH on the sorption of europium and uranium since the pH profile at SWSA-6 is not well known. Because organic contaminants could also be present in some SWSA-6 groundwaters, the effect of several organic compounds on europium sorption was also tested.

The tests completed and described in this report are considered to be primarily scouting tests that help define the behavior of these radionuclide contaminants in typical SWSA-6 saturated zone soil/groundwater systems. Sorption ratio values for these five radionuclide contaminants which may be suitable for initial migration modeling purposes are presented in Sect. 4.

2. MATERIALS AND METHODS

2.1 SOILS AND GROUNDWATER

Most of the experiments were carried out with a fraction of an ~18-kg sample of soil which was obtained from the bottom of a freshly opened

SWSA-6 trench (located at N 17,500, E 24,650). This sample may be representative of the SWSA-6 saturated zone soils; at least, it was taken from below the leached, unsaturated soil region. After the sample was received in the laboratory on February 10, 1986, the soil was air dried and then screened without crushing to obtain fine material for the sorption tests. Approximately 2 kg of the as-received material passed a 20-mesh screen. This -20-mesh soil fraction was homogenized in a V-blender and used in the sorption experiments. This soil is identified as "SWSA-6 soil," or simply "soil," in this report. Some of the +20-mesh material was used to stabilize the groundwater, as described later.

A few experiments were carried out with small samples of three well-characterized SWSA-6 soils received from S. Y. Lee (ORNL Environmental Sciences Division). These samples are identified in this report as "claystone," "sandstone," and "sandstone plus." The information received with the samples characterized them as follows: claystone, <2 mm; sandstone with manganese coatings, 2-5 mm; and sandstone with shale partings and clay films. These soils are further described in Lietzke and Lee (1986).

The groundwater used in the experiments was from an ~4.5-gal sample of water from well PS-8, which was received in the laboratory on February 10, 1986, in a 5-gal plastic bottle. As received, the groundwater pH was ~8.1. To stabilize the groundwater, about 1 to 2 kg of the +20-mesh soil material was added to the 5-gal bottle, and the soil and groundwater were occasionally mixed by shaking the bottle. The pH of samples of groundwater not stabilized by soil tended to drift upward with time. The presence of the soil components stabilized the groundwater pH at ~7.0 to 7.2 in tests conducted for various times at three water/soil ratios (Table 2.1). Presumably, calcite in the soil was replenishing dissolved CO_2 lost to the atmosphere. Groundwater samples for use in the experiments were withdrawn from the top of the solution in the 5-gal bottle after allowing the soil to settle overnight or longer.

Table 2.1. Measurements of pH of SWSA-6 wellwater/soil mixtures

Contact time (h)	pH at a wellwater/soil (mL/g) ratio of 5	3.3	1
2.5	7.1	7.1	7.1
6	7.2	7.2	7.1
23	7.2	7.2	7.1
47	7.2	7.2	7.0
71	7.2	7.2	7.0

2.2 BATCH CONTACT METHODOLOGY

Batch contact methodology was used in all the radionuclide sorption experiments. For the soil/groundwater contact, 2.0 g of the respective soil and 10.0 mL of the spiked and traced groundwater were placed in a 15-mL graduated glass centrifuge tube on a Burrell wrist-action shaker. These were mixed at ~170 strokes/min for the desired time. This method of contact afforded continuous mixing with a minimum of shear forces or violent agitation, which could alter the soil surface or particle size. All tests were carried out at room temperature, ~24°C. The groundwaters for use in the experiments were spiked to the desired element concentration by addition of one or more stable isotope compounds and were traced by the addition of ~15,000-counts per minute activity of one radionuclide. The compounds used to spike the groundwater were $CsNO_3$, $CoCl_2$, $Eu(NO_3)_3$, $SrCl_2$, and $UO_2(NO_3)_2$. The radioactive tracers were $^{137}CsCl$, $^{60}CoCl_2$, $^{155}EuCl_3$, $^{89}SrCl_2$, and $^{233}UO_2(NO_3)_2$. In some tests, only one element was present in the spiked and traced groundwater (e.g., natural Cs and ^{137}Cs), while all five elements plus one radionuclide were present in other tests designed to explore the effects of competition for sorption sites. After the contact, the groundwater solution was recovered by centrifugation at ~3000 rpm for 3 to 15 min. The tracer radionuclide was counted using alpha liquid scintillation spectrometry for the ^{233}U and gross gamma counting with an NaI crystal detector for the other radionuclides. The sorption ratio (L/kg),

$$R_s = \frac{\text{element concentration on the solids (mol/kg)}}{\text{element concentration in solution (mol/L)}} ,$$

was calculated from the respective element concentrations. The concentration of the element on the solids was calculated from the difference in the initial and after-contact concentration of the groundwater. All experiments were run in triplicate, and the concentration values and sorption ratios given in the tables in Chap. 3 of this report are the mean ±1 standard deviation of the replicate values. The amount of radioactive tracer used in the tests limited the measurement of sorption ratios to values of ~3000 L/kg or less. A few higher R_s values are recorded in some tables in Chap. 3; however, the precision is poor since, at this high an R_s value, the count rate of the solution was approaching the background count rate.

In two series of tests with europium and uranium, the pH of the soil/groundwater system was deliberately adjusted to more acidic values to study the effect of pH on sorption. For these tests, a mixture of ~125 g of soil and ~650 mL of groundwater was adjusted with HCl to the desired pH. The pH was periodically readjusted to the desired value by the addition of more HCl until the pH was stable. The pH-adjusted soil and groundwater were then separated by decantation and filtration and used in sorption tests, as described above.

In one series of tests, organic compounds were added to the groundwater to explore the effect of potential complexing reagents on the sorption of europium. The reagents used were naphthalene (typical of scintillation fluids), EDTA (disodium ethylenediaminetetraacetate, typical of complexing reagents), TBP (tributyl phosphate, used in many solvent extraction steps), and toluene and chloroform (typical waste site organic contaminants).

3. RESULTS

3.1 RADIONUCLIDE SORPTION ISOTHERMS

Sorption isotherms were run to measure the element sorption ratios as a function of concentration. In addition, parallel isotherms were run in the presence of all the elements at the highest concentration tested to investigate competition for sorption sites. Prior to running

the isotherm tests, preliminary tests were run at the highest element concentration for various lengths of time to explore the time needed for the test systems to reach steady-state conditions.

3.1.1 Cesium

In the preliminary tests, the sorption of cesium was so complete that the ^{137}Cs activity remaining in solution after contact was near the background count rate after only 24-h contact. Therefore, the sorption isotherms were run with a 24-h contact time. The isotherm data (Table 3.1) show that the sorption of cesium from solutions with initial concentrations of Cs^+ of 10^{-3} to 10^{-10} mol/L were all close to the measurable sorption ratio limit of approximately >3000 L/kg. Also, the addition of the other elements to the cesium-traced groundwater did not measurably reduce the cesium sorption ratio values; that is, there was no evidence of competition for cesium sorption sites.

3.1.2 Cobalt

The results of the preliminary tests suggested that the cobalt-spiked samples reached a steady-state condition in 2 or 3 d (Table 3.2). A contact time of 3 d was chosen for the sorption isotherm tests with groundwater initially containing 10^{-3} to 10^{-10} mol/L cobalt. The isotherm data (Table 3.3) for either cobalt only or cobalt plus other elements showed considerable data scatter in the replicate samples because of the low count rate of ^{60}Co remaining in solution after contact. Most of the R_s values ranged from ~3000 to ~5000 L/kg. These high values are close to the measurable limit. At the highest initial Co^{2+} concentration of 10^{-3} mol/L, a slightly lower R_s value was measured. This suggests the beginning of saturation of the cobalt sorption sites. Surprisingly, the addition of the other elements did not decrease the cobalt R_s value even at the highest Co^{2+} concentration. Apparently, these additional elements do not compete for cobalt sorption sites.

Table 3.1. Cesium isotherms

Initial groundwater Cs (mol/L)	After 24-h contact			
	pH	Soil Cs (mol/kg)	Groundwater Cs (mol/L)	R_s (L/kg)
Cesium only[a]				
10^{-3}	7.3	(4.99 ± 0.00)E-03	(2.0 ± 0.9)E-06	3347 ± 2054
10^{-5}	7.3	~5 E-05	At detection limit[b]	>3000
10^{-7}	7.3	~5 E-07	At detection limit	>3000
10^{-9}	7.4	~5 E-09	At detection limit	>3000
10^{-10}	7.4	~5 E-10	At detection limit	>3000
Cesium + others[c]				
10^{-3}	7.3	(4.99 ± 0.00)E-03	(2.1 ± 0.4)E-06	2500 ± 465
10^{-5}	7.4	~5 E-05	At detection limit[b]	>3000
10^{-7}	7.4	~5 E-07	At detection limit	>3000
10^{-9}	7.4	~5 E-09	At detection limit	>3000
10^{-10}	7.4	~5 E-10	At detection limit	>3000

[a]The initial groundwater contained only cesium at the concentrations indicated.

[b]The count rate of ^{137}Cs in solution after contact was near the background count rate; this gave a calculated R_s value of >3000 L/kg. The actual R_s values may have been higher.

[c]The initial groundwater contained cesium at the concentrations indicated plus 1×10^{-3} mol/L each of cobalt, strontium, and uranium and 1×10^{-5} mol/L of europium.

Table 3.2. Cobalt sorption rate

Contact time (h)	After contact[a]			
	pH	Soil Co (mol/kg)	Groundwater Co (mol/L)	R_s (L/kg)
24	7	(4.95 ± 0.00)E-03	(0.96 ± 0.15)E-05	527 ± 77
48	7.1	(4.96 ± 0.00)E-03	(0.69 ± 0.09)E-05	738 ± 108
72	7.0	(4.96 ± 0.00)E-03	(0.76 ± 0.05)E-05	659 ± 43

[a]Initial concentration: 10^{-3} mol/L cobalt.

Table 3.3. Cobalt isotherms

Initial groundwater Co (mol/L)	After 3-d contact			
	pH	Soil Co (mol/kg)	Groundwater Co (mol/L)	R_s (L/kg)
Cobalt only[a]				
10^{-3}	7.3	(4.96 ± 0.00)E-03	(7.6 ± 0.5)E-06	659 ± 43
10^{-5}	7.3	(4.99 ± 0.00)E-05	(1.2 ± 0.6)E-08	6428 ± 4336
10^{-7}	7.3	(4.99 ± 0.00)E-07	(2.0 ± 1.1)E-10	3180 ± 1458
10^{-9}	7.4	(4.99 ± 0.00)E-09	(1.1 ± 0.2)E-12	4658 ± 1148
10^{-10}	7.4	(4.99 ± 0.00)E-10	(1.3 ± 0.1)E-13	3983 ± 410
Cobalt + others[b]				
10^{-3}	7.3	(4.97 ± 0.01)E-03	(6.9 ± 1.2)E-06	741 ± 123
10^{-5}	7.4	(4.99 ± 0.00)E-05	(2.4 ± 0.7)E-08	2355 ± 856
10^{-7}	7.4	(4.99 ± 0.00)E-07	(1.4 ± 0.6)E-10	5133 ± 3441
10^{-9}	7.4	(4.99 ± 0.00)E-09	(2.3 ± 0.5)E-12	2237 ± 502
10^{-10}	7.4	(4.99 ± 0.00)E-10	(1.6 ± 0.6)E-13	3762 ± 1768

[a]The initial groundwater contained only cobalt at the concentrations indicated.

[b]The initial groundwater contained cobalt at the concentrations indicated plus 1×10^{-3} mol/L each of cesium, strontium, and uranium and 1×10^{-5} mol/L of europium.

3.1.3 Europium

As with cesium, the sorption of europium was so great after a 24-h contact that the ^{155}Eu activity in the solution was close to the background level. The R_s values measured in the europium isotherms run with initial groundwater concentrations of 10^{-5} to 10^{-10} mol/L europium (Table 3.4) were all high (~3000 to ~5000 L/kg). The standard deviation for the values was also high, as would be expected since the activity that remained in the groundwater after contact was close to the background level. The sorption ratio values show no effect from europium concentration on the competition for sorption sites by the other elements added in the second isotherm series. Tests were not run with an initial europium concentration higher than 10^{-5} mol/L to avoid complications that could result if precipitation as well as sorption occurred.

Table 3.4. Europium isotherms

Initial groundwater Eu (mol/L)	After 24-h contact			
	pH	Soil Eu (mol/kg)	Groundwater Eu (mol/L)	R_s (L/kg)
Europium only[a]				
10^{-5}	7.4	~5E-05	At detection limit[b]	>3000
10^{-7}	7.3	(4.99 ± 0.00)E-07	(1.7 ± 0.2)E-10	2919 ± 340
10^{-9}	7.4	(4.99 ± 0.00)E-09	(1.8 ± 0.5)E-12	3200 ± 1274
10^{-10}	7.4	(4.99 ± 0.00)E-10	(1.8 ± 0.7)E-13	3239 ± 1102
Europium + others[c]				
10^{-5}	7.3	(4.99 ± 0.00)E-05	(1.0 ± 0.3)E-08	5630 ± 1995
10^{-7}	7.3	(4.99 ± 0.00)E-07	(1.4 ± 0.2)E-10	3602 ± 683
10^{-9}	7.3	(4.99 ± 0.00)E-09	(1.3 ± 0.8)E-12	4923 ± 2113
10^{-10}	7.3	(4.99 ± 0.00)E-10	(1.1 ± 0.4)E-13	5886 ± 2964

[a]The initial groundwater contained only europium at the concentrations indicated.

[b]The count rate of ^{155}Eu in solution after contact was near the background count rate; this gave a calculated R_s value of >3000 L/kg. The actual R_s value may have been higher.

[c]The initial groundwater contained europium at the concentrations indicated plus 1×10^{-3} mol/L each of cesium, cobalt, strontium, and uranium.

3.1.4 Strontium

Initial tests (Table 3.5) showed that the strontium-spiked samples had apprently reached a steady-state condition in 24 h or less. Therefore, the sorption isotherms (Table 3.6) were run with a 24-h contact time. With groundwater containing only strontium, the sorption ratio was constant (about 78 L/kg) for samples covering a five order-of-magnitude range of initial Sr^{2+} concentrations (10^{-5} to 10^{-10} mol/L). The sorption ratio fell to 47 L/kg at the highest strontium concentration. When the other elements were added to the groundwater, the sorption ratio values were all depressed to values between 30 and 40 L/kg. This behavior suggests that one or more of the added elements was competing with Sr^{2+} for sorption sites.

Table 3.5. Strontium sorption rate

Contact time (h)	After contact[a]			
	pH	Soil Sr (mol/kg)	Groundwater Sr (mol/L)	R_s (L/kg)
24		(4.52 ± 0.00)E-03	(9.56 ± 0.20)E-05	47.3 ± 1.1
48		(4.52 ± 0.00)E-03	(9.66 ± 0.03)E-05	46.7 ± 0.2
72	7.2	(4.51 ± 0.01)E-03	(9.77 ± 0.13)E-05	46.2 ± 0.7
168	7.3	(4.51 ± 0.01)E-03	(9.85 ± 0.18)E-05	45.8 ± 0.9

[a]Initial concentration: 10^{-3} mol/L strontium.

Table 3.6. Strontium isotherms

Initial groundwater Sr (mol/L)	After 24-h contact			
	pH	Soil Sr (mol/kg)	Groundwater Sr (mol/L)	R_s (L/kg)
Strontium only[a]				
10^{-3}		(4.52 ± 0.01)E-03	(9.56 ± 0.20)E-05	47.3 ± 1.1
10^{-5}	7.4	(4.69 ± 0.00)E-05	(6.13 ± 0.02)E-07	76.6 ± 0.3
10^{-7}	7.4	(4.70 ± 0.00)E-07	(5.98 ± 0.05)E-09	78.6 ± 0.9
10^{-9}	7.4	(4.70 ± 0.00)E-09	(5.98 ± 0.09)E-11	78.7 ± 1.2
10^{-10}	7.4	(4.70 ± 0.00)E-10	(5.99 ± 0.09)E-12	78.5 ± 1.3
Strontium + others[b]				
10^{-3}	7.2	(4.32 ± 0.00)E-03	(1.36 ± 0.01)E-04	31.7 ± 0.2
10^{-5}	7.2	(4.46 ± 0.01)E-05	(1.08 ± 0.01)E-06	41.5 ± 0.5
10^{-7}	7.2	(4.29 ± 0.01)E-07	(1.41 ± 0.01)E-08	30.4 ± 0.3
10^{-9}	7.3	(4.37 ± 0.02)E-09	(1.25 ± 0.04)E-10	34.9 ± 1.3
10^{-10}	7.4	(4.38 ± 0.01)E-10	(1.24 ± 0.02)E-11	35.1 ± 0.6

[a]The initial groundwater contained only strontium at the concentrations indicated.

[b]The initial groundwater contained strontium at the concentrations indicated plus 1×10^{-3} mol/L each of cesium, cobalt, and uranium and 1×10^{-5} mol/L of europium.

3.1.5 Uranium

The sorption behavior of uranium was markedly different from that of the other elements. The preliminary tests with groundwater spiked with 10^{-3} mol/L uranium (Table 3.7) showed only low sorption ratio values of ~2 L/kg and suggested that steady-state conditions might not have been reached by the longest contact time studied (168 h), although the additional decrease in the solution uranium concentration with time was small. Because of time constraints for completion of this work, longer contact times were not explored. The sorption isotherms (Table 3.8) showed a strong dependence of the sorption ratio on the uranium concentration. At lower uranium concentrations, the sorption ratio increased to ~50 to ~60 L/kg for the uranium-only tests and to ~40 to ~50 L/kg when the additional elements were present. The results suggest that the uranium sorption sites may have been nearly saturated at the highest uranium concentrations. The results also suggest that one or more of the additional elements may be competing with uranium for sorption sites.

Table 3.7. Uranium sorption rate

Contact time (h)	After contact[a]			
	pH	Soil U (mol/kg)	Groundwater U (mol/L)	R_s (L/kg)
24	7.5	(1.36 ± 0.06)E-03	(7.28 ± 0.12)E-04	1.87 ± 0.11
48	7.4	(1.39 ± 0.04)E-03	(7.23 ± 0.07)E-04	1.92 ± 0.07
72	7.4	(1.48 ± 0.01)E-03	(7.03 ± 0.02)E-04	2.11 ± 0.02
96	7.4	(1.46 ± 0.05)E-03	(7.09 ± 0.11)E-04	2.05 ± 0.10
168	7.3	(1.54 ± 0.04)E-03	(6.93 ± 0.07)E-04	2.22 ± 0.08

[a]Initial concentration: 10^{-3} mol/L uranium.

Table 3.8. Uranium isotherms

Initial groundwater U (mol/L)	After 7-d contact			
	pH	Soil U (mol/kg)	Groundwater U (mol/L)	R_s (L/kg)
Uranium only[a]				
10^{-3}	7.3	(1.54 ± 0.04)E-03	(6.93 ± 0.07)E-04	2.22 ± 0.08
10^{-5}	7.4	(4.53 ± 0.05)E-05	(8.87 ± 0.22)E-07	51.4 ± 1.4
4×10^{-6}	7.4	(1.85 ± 0.00)E-05	(2.93 ± 0.07)E-07	63.4 ± 1.7
Uranium + others[b]				
10^{-3}	7.3	(1.56 ± 0.03)E-03	(6.87 ± 0.07)E-04	2.28 ± 0.07
10^{-5}	7.1	(4.45 ± 0.03)E-05	(1.10 ± 0.06)E-06	40.6 ± 2.4
4×10^{-6}	7.1	(1.81 ± 0.00)E-05	(3.80 ± 0.03)E-07	47.6 ± 0.4

[a]The initial groundwater contained only uranium at the concentrations indicated.

[b]The initial groundwater contained uranium at the concentrations indicated plus 1×10^{-3} mol/L each of cesium, cobalt, and uranium and 1×10^{-5} mol/L of europium.

3.2 COMPARISON OF SOILS

The radionuclide sorption properties of four different soil samples from SWSA-6 were compared to explore the potential differences that may exist for soils in various areas or at different depths in SWSA-6. The site soil mineralogy is complex and may be locally variable (Boegly et al. 1985). Therefore, it seemed important to examine various solid samples in addition to the sample from the bottom of a trench used in the other sorption isotherm tests. Three well-characterized SWSA-6 soil samples were obtained from S. Y. Lee. Since only limited quantities of these new soils were avilable, batch contact tests were run in triplicate only at the highest element concentration used in the preceding sorption isotherm experiments.

The sorption ratios for the five elements are compared (Table 3.9) for these three well-characterized soils as well as for the soil used in the other tests. The solution pH was not adjusted during the contact

Table 3.9. Sorption behavior of four SWSA-6 soils[a]

Element	Soil[b]		Claystone[c]		Sandstone[d]		Sandstone plus[e]	
	pH	R_s (L/kg)	pH	R_s (L/kg)	pH	R_s (L/kg)	pH	R_s (L/kg)
Cs(I)	7.3	3347 ± 2054	5.5	5035 ± 2356	5.9	1446 ± 456	5.1	151 ± 11
Co(II)	7.3	659 ± 43	6.0	229 ± 24	6.3	234 ± 28	5.8	199 ± 10
Eu(III)	7.3	>3000	5.8	>3000	6.2	>3000	5.5	>3000
Sr(II)	7.4	47.3 ± 1.1	5.7	133 ± 5	6.1	39.2 ± 1.6	5.0	49.5 ± 2.7
U(VI)	7.3	2.22 ± 0.08	6.7	6.76 ± 0.30	6.9	4.35 ± 0.31	6.7	20.1 ± 0.7

[a]Groundwater (pH 7.3) was spiked to 10^{-3} mol/L of cesium, cobalt, strontium, or uranium or 10^{-5} mol/L of europium and contacted with 2 g of the respective soil for 168 h at room temperature (~24°C). The pH was measured after contact.

[b]Soil sample from bottom of trench (soil used in all other tests).

[c]Claystone, <2 mm; from S. Y. Lee.

[d]Sandstone with manganese coatings, 2-5 mm; from S. Y. Lee.

[e]Sandstone with shale partings and clay films; from S. Y. Lee.

period to allow the various soils to express their native acidity. All of the new soils resulted in more acidic conditions, with many pH values being between 5 and 6 after contact. Major differences in sorption behavior can be seen. Cesium sorption ratio values were highly dependent upon the soil sample and ranged from ~150 L/kg with sandstone plus to ~5000 L/kg with claystone. Cobalt showed less sensitivity, and the sorption ratios ranged only from ~200 L/kg with the sandstone plus to ~660 L/kg with the original soil. Europium was highly sorbed by all the soils, and the ^{155}Eu activity in solution was reduced to near the background rate. Strontium sorption showed little variability with soil sample, ranging from R_s values of ~40 L/kg with sandstone to ~130 L/kg with claystone. Uranium sorption ratio values varied by an order of magnitude, from ~2 L/kg with the original soil to ~20 L/kg with sandstone plus.

These scouting tests were conducted only to explore the possible variability of sorption behavior which might be seen with samples of SWSA-6 soil and do not afford an explanation of the differences observed in the sorption ratio values in Table 3.9. The sorption of elements can be profoundly influenced by changes in speciation of solubility resulting from pH changes. Also, different minerals or sorptive phases present in the soils could be selective for certain elements. The present data are sufficient to show only that soils in the SWSA-6 site are markedly different in sorptive properties and that this variability will have to be considered when modeling radioactivity release rates from the site.

3.3 EFFECT OF pH

The pH, or acidity, of the groundwater is one of the primary geochemical parameters that establish the stable solid phase and speciation of soluble forms of elements. As such, the test pH may be an important variable that affects the sorption ratio measured. Since the pH values of the soil/groundwater system(s) at SWSA-6 are not well defined (Boegly et al. 1985), tests were run to span the possible range of pH values that could be encountered at SWSA-6 in the unsaturated, as well as the saturated, zones.

3.3.1 Europium

The europium sorption ratio proved to be sensitive to the test pH (Table 3.10). The sorption ratio increased from ~100 L/kg at pH ~4.3 to ~3000 L/kg at pH ~6.7 or higher. Lower R_s values were observed at the highest europium concentration used, 10^{-3} mol/L, presumably because of loading effects on the sorbent.

Table 3.10. Europium sorption isotherms as a function of pH

Initial groundwater Eu (mol/L)	After 168-h contact[a]			
	pH	Soil Eu (mol/kg)	Groundwater Eu (mol/L)	R_s (L/kg)
pH ~4.3				
10^{-3}	4.2	(4.61 ± 0.01)E-03	(7.85 ± 0.13)E-05	58.8 ± 1.1
10^{-5}	4.3	(4.74 ± 0.00)E-05	(5.16 ± 0.06)E-07	91.9 ± 1.1
10^{-7}	4.3	(4.76 ± 0.01)E-07	(4.84 ± 0.19)E-09	98.4 ± 4.0
10^{-9}	4.4	(4.75 ± 0.01)E-09	(4.98 ± 0.13)E-11	95.4 ± 2.6
10^{-10}	4.4	(4.76 ± 0.00)E-10	(4.84 ± 0.19)E-12	98.5 ± 4.3
pH ~5.6				
10^{-3}	5.3	(4.80 ± 0.01)E-03	(4.10 ± 0.15)E-05	117 ± 5
10^{-5}	5.6	(4.95 ± 0.01)E-05	(1.10 ± 0.28)E-07	487 ± 141
10^{-7}	5.7	(4.95 ± 0.01)E-07	(1.06 ± 0.07)E-09	467 ± 32
10^{-9}	5.6	(4.95 ± 0.01)E-09	(1.09 ± 0.14)E-11	461 ± 65
10^{-10}	5.7	(4.96 ± 0.01)E-10	(8.90 ± 1.91)E-13	580 ± 109
pH ~6.7				
10^{-3}	6.4	(4.96 ± 0.00)E-03	(7.7 ± 0.4)E-06	646 ± 38
10^{-5}	6.7	(4.99 ± 0.00)E-05	(1.1 ± 0.7)E-08	6326 ± 5004
10^{-7}	6.7	(4.99 ± 0.00)E-07	(1.7 ± 1.1)E-10	4115 ± 1937
10^{-9}	6.8	(4.99 ± 0.00)E-09	(1.7 ± 0.4)E-12	3054 ± 564
10^{-10}	6.8	(4.99 ± 0.00)E-10	(1.5 ± 0.3)E-13	3478 ± 765
pH ~7.4 (from Table 3.4)				
10^{-7}	7.3	(4.99 ± 0.00)E-07	(1.7 ± 0.2)E-10	2919 ± 340
10^{-9}	7.4	(4.99 ± 0.00)E-09	(1.8 ± 0.5)E-12	3200 ± 1274
10^{-10}	7.4	(4.99 ± 0.00)E-10	(1.8 ± 0.7)E-13	3239 ± 1102

3.3.2 Uranium

The uranium sorption ratio showed a complex behavior with respect to pH (Table 3.11). The R_s values increased from ~250 L/kg at pH ~4.2 to ~3000 L/kg at pH ~5.5. The R_s values then decreased to ~50 L/kg at pH ~7.4. This behavior is consistent with the chemistry of U(VI) in groundwaters (Langmuir 1978). At pH 4.2 the species is primarily UO_2^{2+}, while at pH 5.5, neutral species such as UO_2CO_3 become important. A pH of 5.5 is near the isoelectric point and the minimum solubility of U(VI) as a function of pH (Baes and Mesmer 1976). Thus, it is reasonable for the R_s values to be at a maximum near pH 5.5. At still higher pHs, such as 7.4, anionic carbonate complexes such as $UO_2(CO_3)_3^{4-}$ become important. Anions generally are poorly sorbed on geologic materials; so a decrease in the R_s values at the higher pHs tested also seems reasonable.

Table 3.11. Uranium sorption isotherms as a function of pH

Initial groundwater U (mol/L)	After 168-h contact			
	pH	Soil U (mol/kg)	Groundwater U (mol/L)	R_s (L/kg)
pH ~4.2				
10^{-3}	4.1	(3.89 ± 0.04)E-03	(2.21 ± 0.08)E-04	17.6 ± 0.8
10^{-5}	4.2	(4.90 ± 0.09)E-05	(2.10 ± 0.09)E-07	235 ± 11
4×10^{-6}	4.3	(1.97 ± 0.00)E-05	(6.68 ± 0.36)E-08	296 ± 17
pH ~5.5				
10^{-3} [a]				
10^{-6}	5.6	(4.99 ± 0.00)E-05	(1.36 ± 0.09)E-08	3670 ± 241
4×10^{-6}	5.4	(2.00 ± 0.00)E-05	(7.20 ± 2.00)E-09	2986 ± 760
pH ~6.2				
10^{-3} [a]				
10^{-6}	6.2	(4.97 ± 0.02)E-05	(6.50 ± 3.20)E-08	1172 ± 852
4×10^{-6}	6.3	(1.98 ± 0.02)E-05	(1.93 ± 0.39)E-08	1059 ± 183
pH ~7.4 (from Table 3.8)				
10^{-3}	7.3	(1.54 ± 0.04)E-03	(6.93 ± 0.07)E-04	2.22 ± 0.08
10^{-5}	7.4	(4.53 ± 0.05)E-05	(8.87 ± 0.22)E-07	51.4 ± 1.4
4×10^{-6}	7.4	(1.85 ± 0.00)E-05	(2.93 ± 0.07)E-07	63.4 ± 1.7

[a]A precipitate formed when uranium was added to these solutions at a concentration of 10^{-3} mol/L.

3.4 EFFECT OF ORGANIC REAGENTS

Sorption tests were run with europium in the presence of a number of organic reagents typical of those that might be encountered in SWSA-6. Locations identified as solvent auger holes exist on SWSA-6 maps, but apparently no information is available as to the solvents or method of disposal used (Solomon 1986). The organics tested (at ten times the europium concentration) were naphthalene, EDTA, TBP, toluene, and chloroform. Their effect on europium was examined since europium is the largest single radioactive contaminant discharged to SWSA-6 (Beogly et al. 1985). The results (Table 3.12) were surprising. None of the organics had any measurable effect on the europium sorption ratio at this pH. This provisional finding is highly favorable to the predicted future ability of SWSA-6 to retard the release of europium since the results suggest that at least these organics may not complex with europium and decrease the high (>3000 L/kg) sorption ratio.

Table 3.12. Effect of organic reagents on europium sorption

Organic reagent (mol/L)	After contact[a] Soil Eu (mol/kg)	Groundwater Eu (mol/L)	R_s (L/kg)
Naphthalene	~5E-07	At detection limit[b]	>3000
EDTA	(5.00 ± 0.00)E-07	(1.6 ± 0.7)E-10	3626 ± 1465
TBP	~5E-07	At detection limit[b]	>3000
Toluene	~5E-07	At detection limit[b]	>3000
Chloroform	~5E-07	At detection limit[b]	>3000

[a]The initial groundwater contained 10^{-7} mol/L europium. The organic reagents were then added to the groundwater at a concentration of 10^{-6} mol/L. The contact time was 168 h. The final pHs were 7.4 to 7.5.

[b]The count rate of the ^{155}Eu in solution after contact was near the background count rate; this gave a calculated R_s value of >3000 L/kg. The actual value may have been higher.

4. DISCUSSION

4.1 SORPTION ISOTHERM TESTS

A number of general patterns were observed in the sorption behavior of the radionuclides tested. Cesium, cobalt, europium, and strontium sorption behaviors frequently were similar in some respects, while uranium often showed different behavior. General observations derived from the sorption isotherm tests are as follows:

1. Sorption rate - In the initial sorption rate tests designed to select the minimum test contact time that appeared to yield steady-state sorption ratio values, cesium, cobalt, europium, and strontium appeared to reach steady state in 24 h or less, while the uranium sorption ratio continued to increase slightly over a one-week period.

2. Sorption ratio - In the linear portion of the sorption isotherms run at near-neutral pHs, which may be typical of the SWSA-6 saturated zone, cesium, cobalt, and europium R_s values were near the analytical measurement limit of >3000 L/kg. Strontium and uranium R_s values were lower and ranged from 50 to 75 L/kg. Sorption ratios as high as 3000 L/kg may result in retardation (reduced mobility) of the soluble species within the SWSA-6 site for environmentally favorable lengths of time.

3. Sorption capacity - In the cases of cobalt, strontium, and uranium, the sorption ratio values at the highest concentration of the element used in the isotherm tests (10^{-3} mol/L) were lower than those at the lower concentrations (10^{-5} to 10^{-10} mol/L). This decreased sorption capability presumably was due to saturation of the sorption sites (loading of the sorbent); isotherms typically turn over (the sorption ratio decreases) at higher concentrations of the element in solution. Cesium and europium sorption values were near the measurable limit of >3000 L/kg and showed no significant decrease in tests at 10^{-3}-mol/L concentration. Absence of site loading effects at solution concentrations as high as 10^{-5} to 10^{-3} mol/L may represent unusually high sorption capacity in the SWSA-6 soils and thus favorable capability of the site to retain appreciable quantities of these radionuclides.

4. Sorption competition - In the sorption isotherm tests where the other four elements were added to the radionuclide-traced element, little evidence for competition for sorption sites was observed in the cases of cesium, cobalt, and europium. Only the strontium and uranium isotherms suggested competition for sorption sites, as evidenced by decreased R_s values in the linear portion of the isotherm. Even for these two elements,

the R_s value was reduced only by one-half or less. This is a surprising result and suggests that at least some of the elements may have discrete or unique sorption sites on specific mineral phases. More evidence of competition for sorption sites had been anticipated. This finding suggests that the SWSA-6 sorption capacity for these radionuclides may not be easily compromised by the presence of other solution species.

4.2 SCOUTING TESTS

After completion of the sorption isotherm tests under steady-state conditions and saturated zone-relevant geochemical parameters, a few additional tests were completed to explore the effects of several parameters on the sorption behavior of selected elements. Significant observations from these tests are as follows:

1. Various soils - The geology of the SWSA-6 site is complex and poorly characterized (Boegly et al. 1985), and a variety of soil types exists at different locations and depths (Lietzke and Lee 1986). Sorption tests were run at a 10^{-3}-mol/L concentration with three different well-characterized soils for comparison with the large batch of soil used in the isotherm tests. Major differences were observed in the measured sorption ratio for the some of the elements onto the different soils. Cesium sorption ratios ranged from ~150 to ~5000 L/kg; cobalt, from ~200 to ~650 L/kg; strontium, from ~40 to ~130 L/kg; and uranium, from ~2 to ~20 L/kg. Europium sorption ratios were <3000 L/kg, near the analytical detection limit, for all soils. Most of the well-characterized soils changed the pH of the poorly buffered groundwater to pHs between 5 and 6. Apparently, these soils are mineralogically different from the soil from the bottom of a trench since they altered the test pH as well as the sorption behavior. These scouting test results suggest that modeling the mobility of radionuclides in the unsaturated zone could be complex because of the variability of soils and groundwater parameters which might exist.

2. Effect of pH - The effect of the test pH was systematically studied only for europium and uranium, the major contaminants present in SWSA-6. The R_s value for both elements was sensitive to the pH. Europium sorption decreased from >3000 L/kg at near-neutral pH to ~100 L/kg at pH ~4.3. Uranium sorption displayed a maximum R_s value of ~3000 L/kg at pH ~5.5, and the R_s value decreased at lower or higher pHs. For these elements at least, defensible mobility modeling may require knowledge of the soil/groundwater system pH along the release pathway.

3. Effect of organic reagents - The effect of several organic reagents that could be present in the SWSA-6 site were explored only for europium sorption. No effect was observed at this pH; all R_s values were near the detection limit of 3000 L/kg. This surprising result is highly favorable to demonstrating the ability of the SWSA-6 site to retain europium radionuclides. The finding suggests that, in mobility modeling, reduced sorption (increased mobility) due to the presence of unknown organics in SWSA-6 might not have to be considered.

4.3 RECOMMENDED SORPTION RATIO VALUES FOR MOBILITY MODELING

In Table 4.1, sorption ratio values are recommended for use in preliminary mobility or migration modeling for the five radionuclides in the saturated zone (pH 7.0 to 7.5) at the SWSA-6 site. It should be clearly understood that the very limited experimental work described in this report has yielded information of only a preliminary nature. The batch contact methodology used does not permit evaluation of important sorption aspects such as sorption/desorption on disequilibrium (hysteresis), multiple soluble species of radionuclides, or multiple forms of radionuclides (colloidal as well as dissolved). Thus, the sorption ratio values recommended could be either conservative or nonconservative in some possible situations. If one or more radionuclides appear critical to modeling the SWSA-6 performance, then additional sorption tests, including chromatographic columns, may be needed. With this qualification then, the R_s values are presented in Table 4.1.

The provisional data obtained in the initial tests indicate that cesium, cobalt, and europium may be strongly sorbed and their mobility strongly retarded in the SWSA-6 saturated zone. Strontium and uranium are not as strongly sorbed, but appreciable retardation may be provided by sorption processes. Uranium sorption, in particular, seemed chemically complex and could be more difficult to predict.

Table 4.1. Provisionally recommended radionuclide sorption ratios for the SWSA-6 saturated zone (pH 7.0 to 7.5)

Element	R_s (L/kg)	Comments
Cs	3000	May be lower in leached (unsaturated) zone soils.
Co	3000	May be lower in leached (unsaturated) zone soils.
Eu	3000	May be lower at lower pHs.
Sr	30	Value accommodates site competition.
U	40	Value accommodates site competition; may be higher in leached zone; may be higher at lower pHs.

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